SHUSAKU YAMAMOTO

Japanese Patent (Kokoku) Publication NO. 58-58123

(Translation)

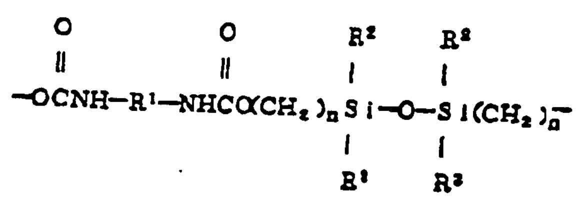
Japanese Patent (Kokoku) Publication for Opposition No. 58-58123

Publication for Opposition Date: December 23, 1983
Application Number: 56-10439
Filing Date: January 26, 1981
Laid-Open Publication Number: 57-122907
Laid-Open Publication Date: July 31, 1982
Inventors: Masao ABE et al.

Gas Separation Film

Claims

A gas separation film, consisting of poly(urethane/disiloxane) having a repeating unit represented by general formula:



(wherein R^1 is a divalent aliphatic group or aromatic group, R^2 is independently a monovalent alkyl group or aromatic group, and n is an integer of 1 through 4).

Detailed Description of the Invention

The present invention relates to a gas separation film consisting of polyurethane including a disiloxane structure.

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Recently, gas separation, especially oxygen enrichment of air by an organic polymer film has been a subject of attention from the viewpoint of saving resources and energy. Conventionally known films for oxygen enrichment have an excessively low transmission speed of oxygen or an excessively small transmission coefficient ratio relative to nitrogen, and therefore are not suitable for oxygen enrichment on an industrial scale. For example, polydimethyl siloxane has an oxygen transmission coefficient in the order of the 10^{-8} $cm^2(STP)\cdot cm/cm^2\cdot sec\cdot cmHg$, which is the highest among the coefficients of the conventionally known polymer films. However, polydimethyl siloxane, which has a transmission coefficient ratio relative to nitrogen of about 2 at most, is inferior in the selective transmittance or separability of oxygen, and thus requires a great number of treatment steps in order to produce oxygen at a high concentration. Therefore, polydimethyl siloxane is not practical in terms of both apparatus requirements and costs. A polydimethyl siloxane film also has a low mechanical strength, and thus needs to be relatively thick. For this reason, the transmission speed of polydimethyl siloxane film cannot be increased although the transmission coefficient is large.

Accordingly, Japanese Patent Publication for Opposition No. 47-51715 proposes an oxygen enrichment film formed of polyvinyl trimethylsilane. The transmission coefficient ratio of oxygen relative to nitrogen of the film is twice that of polydimethyl siloxane, but the film is inferior in the resistance against chemicals and is likely to be deteriorated by contaminants in the air, oil from pumps or the like. United States Patent

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No. 3,189,662 discloses a polysiloxane-polycarbonate block copolymer. This copolymer is also inferior in the resistance against chemicals due to the polycarbonate structure included.

As a result of active studies on gas separation films which are superior in the selective transmittance of oxygen, resistance against chemicals, mechanical strength and the like, the present inventors found that a gas separation film fulfilling the above-described conditions can be produced by introducing a disiloxane structure into a main chain of polyurethane, and thus made the present invention.

The gas separation film according to the present invention consist of poly(urethane/disiloxane) having a repeating unit represented by general formula:

$$-O\overset{\overset{\displaystyle O}{\|}}{C}NH-R^1-NH\overset{\overset{\displaystyle O}{\|}}{C}O(CH_2)_n\underset{\underset{\displaystyle R^2}{|}}{\overset{\overset{\displaystyle R^2}{|}}{Si}}-O-\underset{\underset{\displaystyle R^2}{|}}{\overset{\overset{\displaystyle R^2}{|}}{Si}}(CH_2)_n- \qquad (I)$$

(wherein R^1 is a divalent organic group, R^2 is independently an alkyl group or aromatic group, and n is an integer of 1 through 4).

In general formula (I), R^1 is a divalent organic group, preferably an aliphatic group or an aromatic group. The aromatic group may be bonded via a hetero atom. Examples of R^1 are expressed by:

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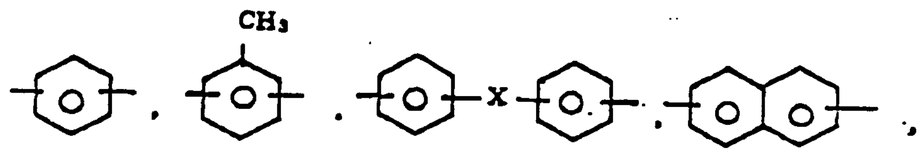

$(CH_2)_6$- and the like, where X is a divalent organic bonding group, i.e., a divalent group which can include a valence bond, alkylene group or a hetero atom. Examples of such a divalent group are $-CH_2-$, $-C(CH_3)_2-$, -O-, -S- and the like.

R^2 is a monovalent alkyl group or an aromatic group. The alkyl group preferably has a carbon number of 1 through 4. An especially preferable example of R^2 is a methyl group or a phenyl group. A disiloxane structure contains four R^2, but all the R^2 are not necessarily identical with one another.

Poly(urethane/disiloxane) having a repeating unit represented by general formula (I) is obtained by causing reaction of the following materials in an appropriate organic solvent with the addition of heat: (i) diisocyanate represented by general formula:

$$OCN-R^1-NCO$$

(R^1 is identical as the above-described material), and (ii) disiloxane-based diol represented by general formula:

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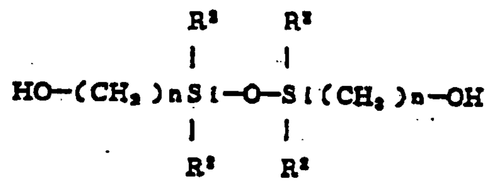

(III)

(R^2 and n are identical as the above-described materials).

In diisocyanate represented by general formula (II), R^1 is an above-described material. Exemplary preferable diisocyanates include tolylenediisocyanate, phenylenediisocyanate, diphenylmethanediisocyanate, diphenylpropanediisocyanate, diphenyletherdiisocyanate, naphthalenediisocyanate, hexamethylenediisocyanate, and the like.

In disiloxane-based diol represented by general formula (III), R^2 and n are above-described materials, and can be obtained by a generally known method. The materials represented by general formula (III) are disclosed in United States Patent No. 2,527,591 where n=1, in J. Org. Chem. 25, 1637 (1950) where n=2 and 3, and in United States Patent No. 3,083,219 where n=4.

Used as a reaction solvent for causing reaction of diisocyanate and disiloxane is a material which dissolves both of the materials, is inert to these materials, and dissolves the poly(urethane/disiloxane) to be produced. Exemplary preferable reaction solvents include aprotic polar organic solvents such as dimethylsulfoxide, N-methyl-2-pyrrolidone, N,N-dimethylacetoamide, N,N-dimethylformamide and the like. These materials can be used independently or as a mixture of two or more. Pref-

erably, a mixed solvent of the above-mentioned solvent and an aliphatic or alicyclic ketone, such as methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, or the like is used. Generally, diisocyanate is difficult to be dissolved in the aprotic polar organic solvent, but can be reacted with diol in a homogenous system or a semi-homogenous system by using a mixed solvent with ketone.

The amount of solvent is not specifically limited, but the solvent is used so that the total amount of diisocyanate and disiloxane-based diol is 10 to 50% by weight, preferably 20 to 40% by weight. The temperature of polymerization is usually in the range of 50 to 150°C, and the time period required for the reaction is usually several to several tens of hours. In order to produce a high molecular weight polymer, diisocyanate is used in an amount of a 2 to 45 mol% excess with respect to disiloxane-based diol.

The poly(urethane/disiloxane) produced in this manner usually has a logarithmic viscosity of 0.4 to 1.2, and can be formed into a tough film. The polymer is inert to almost all the organic solvents except for the polar solvents described above as examples of polymerization solvents and some cyclic ethers such as tetrahydrofuran, and thus has a very excellent resistance against chemicals.

The gas separation film according to the present invention can be produced by various methods, but is usually produced in the following manner. Poly(urethane/disiloxane) is dissolved in a solvent for

film liquid to form a uniform film liquid, and the film liquid is caused to flow over an appropriate support to coat the support with the film liquid. Then, the support coated with the film liquid is heated to vaporize the solvent, thus obtaining a uniform film.

The film preferably has a minimum possible thickness in order to increase the transmission speed of the gas but preferably has a maximum possible thickness in terms of mechanical strength. In consideration of these factors, the film thickness is preferably 0.05 to 30 μm. Accordingly, the concentration of the polymer in the film liquid is 10% by weight or less.

Preferably used as the solvent for film liquid is an aprotic polar organic solvent such as dimethylsulfoxide, N-methyl-2-pyrrolidone, N,N-dimethylacetoamide, N,N-dimethylformamide or the like, as in the case of a polymerization solvent. Tetrahydrofuran is also preferable as the solvent for film liquid since it dissolves the poly(urethane/disiloxane) polymer satisfactorily. If necessary, a mixed solvent of the aprotic organic solvent and tetrahydrofuran is also used. The temperature at which the film liquid is heated after being applied to the support varies in accordance with the type of the film liquid. When an aprotic polar organic solvent is used, the temperature is 80 to 140°C, preferably 100 to 120°C. By an especially preferable method, after the solvent is vaporized almost entirely by a temperature in the above-mentioned range, the solvent is heated to about 150°C to be completely vaporized. Tetrahydrofuran which is used as the solvent for film liquid can be va-

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porized at room temperature, and thus a uniform film can be easily produced.

As described above, the gas separation film according to the present invention is formed of polyurethane having a disiloxane structure in a main chain. Owing to the combination of the relatively high oxygen transmission speed of the disiloxane structure, and the excellent selective transmittance of oxygen and the excellent resistance against chemicals of the polyurethane structure, the gas separation film according to the present invention is especially preferable to oxygen enrichment. Due to the great mechanical strength, the gas separation film according to the present invention is optimum for oxygen enrichment of, for example, air, on an industrial scale. The present invention is also applicable for separation of other types of gas.

Hereinafter, examples of the present invention will be described, but the present invention is not limited to these examples. In the following examples, the transmission coefficient P of gas is obtained at 25°C by a high vacuum method, and the separation coefficient α is obtained from the transmission coefficient of the gas/transmission coefficient of nitrogen (P_{N2}) at 25°C.

Example 1

A dimethylsulfoxide (27 g) solution of bis(hydroxyethyl)tetramethyldisiloxane (8.9 g, 0.040 mol) was added to a methyl isobutyl ketone (120 g) solution of diphenylmethanediisocyanate (13.0 g, 0.052 mol), and heated while being stirred. The viscosity was gradually increased. The reaction was performed

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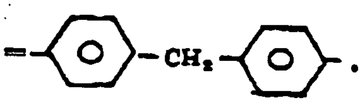
at 100°C for 5 hours, thus obtaining a very viscous solution. The solution was put into a great amount of water to deposit a polymer, which was pulverized in water. After the resultant material was left overnight, the polymer was filtered and vacuum-dried at 80°C for 10 hours. The resultant polymer had a repeating unit represented by general formula (I), where

R^1 = 

R^2=CH_2 and n=2, and a logarithmic viscosity of 0.88 (N-methyl-2-pyrrolidone, 30°C, 0.5 g/dl; hereinafter, the logarithmic viscosity is measured under the same conditions).

A 5% by weight tetrahydrofuran solution was formed including the polymer and caused to flow over a tin-plated board. Then, the board was left at room temperature for 3 days to vaporize the solvent. Then, tin was dissolved in mercury into amalgam, thereby obtaining a uniform polymer film having a thickness of 10 μm. The gas transmittance of the polymer film was measured by a high vacuum method. The results are shown in Table 1.

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Table 1

Gas transmittance of poly(urethane/disiloxane) film

Gas	Transmittance coefficient P (CC(STP)·cm/cm^2·sec·cmHg)	Separation coefficient α
Hydrogen	2.2×10^{-9}	47
Helium	2.1×10^{-9}	45
Carbon dioxide	1.4×10^{-9}	30
Oxygen	2.8×10^{-10}	6
Argon	1.8×10^{-10}	4
Nitrogen	4.7×10^{-11}	1

As a comparative example, a polyurethane film was prepared in the same manner as in example 1 except that ethyleneglycol (2.7 g, 0.043 mol) was used instead of bis(hydroxyethyl)tetramethyldisiloxane. The gas transmittance of the polyurethane film is shown in Table 2.

Table 2

Gas	Transmittance coefficient P (CC(STP)·cm/cm^2·sec·cmHg)	Separation coefficient α
Hydrogen	2.4×10^{-10}	308
Helium	3.8×10^{-10}	490
Carbon dioxide	2.7×10^{-11}	35
Oxygen	5.8×10^{-12}	7
Argon	2.0×10^{-12}	3
Nitrogen	7.8×10^{-13}	1

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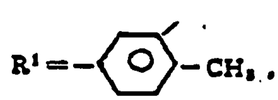
As can be appreciated from the above-described results, the poly(urethane/disiloxane) film according to the present invention increases the selective transmittance of oxygen by 50 times while maintaining a high separation coefficient of oxygen relative to nitrogen. Furthermore, the film according to the present invention is insoluble in almost all the organic solvents except for the aprotic polar organic solvents and tetrahydrofuran, and thus has an excellent resistance against chemicals. Moreover, the film is tough and has a sufficient mechanical strength as indicated by a strength against rupture of 740 kg/cm^2 and an elongation at rupture of 4% which were measured at a tensile rate of 50 mm/min. and a temperature of 25°C.

Example 2

A poly(urethane/disiloxane) polymer was prepared in the same manner as in example 1 except that 2,4-tolylenediisocyanate (7.5 g, 0.043 mol) was used instead of diphenylmethanediisocyanate and that bis(hydroxypropyl)tetramethyldisiloxane (10.0 g, 0.040 mol) was used instead of bis(hydroxyethyl)tetramethyldisiloxane. The resultant polymer is represented by the above general formula, where



R^2=CH_2 and n=3, and has a logarithmic viscosity of 0.76. A film having a thickness of 15 μm was prepared based on the polymer in the same manner as in example 1. The film had a transmission coefficient of oxygen of 3.0×1.0^{-10}

CC(STP)·cm/cm^2·sec·cmHg and a separation coefficient of 5.7.

Example 3

A polymer was prepared in the same manner as in example 1 except that hexamethylenediisocyanate was used instead of diphenylmethanediisocyanate and that bis(hydroxybutyl)tetraphenyldisiloxane was used instead of bis(hydroxyethyl)tetramethyldisiloxane. The resultant polymer is represented by general formula (I) where R^1=-$(CH_2)_6$, R^2=-C_6H_5-, n=4, and has a logarithmic viscosity of 0.61. A film prepared based on the polymer in the same manner as in example 1 had a transmission coefficient of oxygen of 8.2×1.0^{-10} CC(STP)·cm/cm^2·sec·cmHg and a separation coefficient of 3.2.

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(wherein R^1 is a divalent aliphatic group or aromatic group, R^2 is independently a monovalent alkyl group or aromatic group, and n is an integer of 1 through 4).

Detailed Description of the Invention

The present invention relates to a gas separation film consisting of polyurethane including a disiloxane structure.

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Accordingly, Japanese Patent Publication for Opposition No. 47-51715 proposes an oxygen enrichment film formed of polyvinyl trimethylsilane. The transmission coefficient ratio of oxygen relative to nitrogen of the film is twice that of polydimethyl siloxane, but the film is inferior in the resistance against chemicals and is likely to be deteriorated by contaminants in the air, oil from pumps or the like. United States Patent

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No. 3,189,662 discloses a polysiloxane-polycarbonate block copolymer. This copolymer is also inferior in the resistance against chemicals due to the polycarbonate structure included.

As a result of active studies on gas separation films which are superior in the selective transmittance of oxygen, resistance against chemicals, mechanical strength and the like, the present inventors found that a gas separation film fulfilling the above-described conditions can be produced by introducing a disiloxane structure into a main chain of polyurethane, and thus made the present invention.

The gas separation film according to the present invention consist of poly(urethane/disiloxane) having a repeating unit represented by general formula:

$$-\overset{\overset{\displaystyle O}{\|}}{C}ONH-R^1-NH\overset{\overset{\displaystyle O}{\|}}{C}O(CH_2)_n\underset{\underset{\displaystyle R^2}{|}}{\overset{\overset{\displaystyle R^2}{|}}{Si}}-O-\underset{\underset{\displaystyle R^2}{|}}{\overset{\overset{\displaystyle R^2}{|}}{Si}}(CH_2)_n- \qquad (I)$$

(wherein R^1 is a divalent organic group, R^2 is independently an alkyl group or aromatic group, and n is an integer of 1 through 4).

In general formula (I), R^1 is a divalent organic group, preferably an aliphatic group or an aromatic group. The aromatic group may be bonded via a hetero atom. Examples of R^1 are expressed by:

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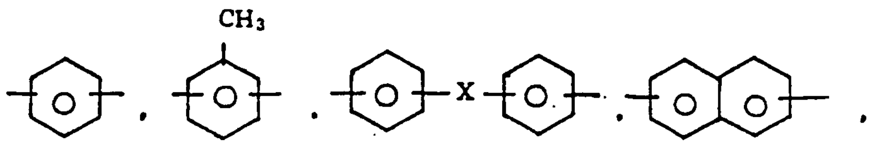

$(CH_2)_6$- and the like, where X is a divalent organic bonding group, i.e., a divalent group which can include a valence bond, alkylene group or a hetero atom. Examples of such a divalent group are $-CH_2-$, $-C(CH_3)_2-$, -O-, -S- and the like.

R^2 is a monovalent alkyl group or an aromatic group. The alkyl group preferably has a carbon number of 1 through 4. An especially preferable example of R^2 is a methyl group or a phenyl group. A disiloxane structure contains four R^2, but all the R^2 are not necessarily identical with one another.

Poly(urethane/disiloxane) having a repeating unit represented by general formula (I) is obtained by causing reaction of the following materials in an appropriate organic solvent with the addition of heat: (i) diisocyanate represented by general formula:

$$OCN-R^1-NCO$$

(R^1 is identical as the above-described material), and (ii) disiloxane-based diol represented by general formula:

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$$HO-(CH_2)_nSi(R^2)_2-O-Si(R^2)_2(CH_2)_n-OH \qquad (III)$$

(R^2 and n are identical as the above-described materials).

In diisocyanate represented by general formula (II), R^1 is an above-described material. Exemplary preferable diisocyanates include tolylenediisocyanate, phenylenediisocyanate, diphenylmethanediisocyanate, diphenylpropanediisocyanate, diphenyletherdiisocyanate, naphthalenediisocyanate, hexamethylenediisocyanate, and the like.

In disiloxane-based diol represented by general formula (III), R^2 and n are above-described materials, and can be obtained by a generally known method. The materials represented by general formula (III) are disclosed in United States Patent No. 2,527,591 where n=1, in J. Org. Chem. 25, 1637 (1950) where n=2 and 3, and in United States Patent No. 3,083,219 where n=4.

Used as a reaction solvent for causing reaction of diisocyanate and disiloxane is a material which dissolves both of the materials, is inert to these materials, and dissolves the poly(urethane/disiloxane) to be produced. Exemplary preferable reaction solvents include aprotic polar organic solvents such as dimethylsulfoxide, N-methyl-2-pyrrolidone, N,N-dimethylacetoamide, N,N-dimethylformamide and the like. These materials can be used independently or as a mixture of two or more. Pref-

erably, a mixed solvent of the above-mentioned solvent and an aliphatic or alicyclic ketone, such as methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, or the like is used. Generally, diisocyanate is difficult to be dissolved in the aprotic polar organic solvent, but can be reacted with diol in a homogenous system or a semi-homogenous system by using a mixed solvent with ketone.

The amount of solvent is not specifically limited, but the solvent is used so that the total amount of diisocyanate and disiloxane-based diol is 10 to 50% by weight, preferably 20 to 40% by weight. The temperature of polymerization is usually in the range of 50 to 150°C, and the time period required for the reaction is usually several to several tens of hours. In order to produce a high molecular weight polymer, diisocyanate is used in an amount of a 2 to 45 mol% excess with respect to disiloxane-based diol.

The poly(urethane/disiloxane) produced in this manner usually has a logarithmic viscosity of 0.4 to 1.2, and can be formed into a tough film. The polymer is inert to almost all the organic solvents except for the polar solvents described above as examples of polymerization solvents and some cyclic ethers such as tetrahydrofuran, and thus has a very excellent resistance against chemicals.

The gas separation film according to the present invention can be produced by various methods, but is usually produced in the following manner. Poly(urethane/disiloxane) is dissolved in a solvent for

film liquid to form a uniform film liquid, and the film liquid is caused to flow over an appropriate support to coat the support with the film liquid. Then, the support coated with the film liquid is heated to vaporize the solvent, thus obtaining a uniform film.

The film preferably has a minimum possible thickness in order to increase the transmission speed of the gas but preferably has a maximum possible thickness in terms of mechanical strength. In consideration of these factors, the film thickness is preferably 0.05 to 30 μm. Accordingly, the concentration of the polymer in the film liquid is 10% by weight or less.

Preferably used as the solvent for film liquid is an aprotic polar organic solvent such as dimethylsulfoxide, N-methyl-2-pyrrolidone, N,N-dimethylacetoamide, N,N-dimethylformamide or the like, as in the case of a polymerization solvent. Tetrahydrofuran is also preferable as the solvent for film liquid since it dissolves the poly(urethane/disiloxane) polymer satisfactorily. If necessary, a mixed solvent of the aprotic organic solvent and tetrahydrofuran is also used. The temperature at which the film liquid is heated after being applied to the support varies in accordance with the type of the film liquid. When an aprotic polar organic solvent is used, the temperature is 80 to 140°C, preferably 100 to 120°C. By an especially preferable method, after the solvent is vaporized almost entirely by a temperature in the above-mentioned range, the solvent is heated to about 150°C to be completely vaporized. Tetrahydrofuran which is used as the solvent for film liquid can be va-

porized at room temperature, and thus a uniform film can be easily produced.

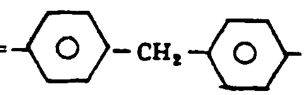
As described above, the gas separation film according to the present invention is formed of polyurethane having a disiloxane structure in a main chain. Owing to the combination of the relatively high oxygen transmission speed of the disiloxane structure, and the excellent selective transmittance of oxygen and the excellent resistance against chemicals of the polyurethane structure, the gas separation film according to the present invention is especially preferable to oxygen enrichment. Due to the great mechanical strength, the gas separation film according to the present invention is optimum for oxygen enrichment of, for example, air, on an industrial scale. The present invention is also applicable for separation of other types of gas.

Hereinafter, examples of the present invention will be described, but the present invention is not limited to these examples. In the following examples, the transmission coefficient P of gas is obtained at 25°C by a high vacuum method, and the separation coefficient α is obtained from the transmission coefficient of the gas/transmission coefficient of nitrogen (P_{N2}) at 25°C.

Example 1

A dimethylsulfoxide (27 g) solution of bis(hydroxyethyl)tetramethyldisiloxane (8.9 g, 0.040 mol) was added to a methyl isobutyl ketone (120 g) solution of diphenylmethanediisocyanate (13.0 g, 0.052 mol), and heated while being stirred. The viscosity was gradually increased. The reaction was performed

at 100°C for 5 hours, thus obtaining a very viscous solution. The solution was put into a great amount of water to deposit a polymer, which was pulverized in water. After the resultant material was left overnight, the polymer was filtered and vacuum-dried at 80°C for 10 hours. The resultant polymer had a repeating unit represented by general formula (I), where

$R^1 =$  ,

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As a comparative example, a polyurethane film was prepared in the same manner as in example 1 except that ethyleneglycol (2.7 g, 0.043 mol) was used instead of bis(hydroxyethyl)tetramethyldisiloxane. The gas transmittance of the polyurethane film is shown in Table 2.

Table 2

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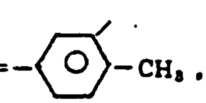
As can be appreciated from the above-described results, the poly(urethane/disiloxane) film according to the present invention increases the selective transmittance of oxygen by 50 times while maintaining a high separation coefficient of oxygen relative to nitrogen. Furthermore, the film according to the present invention is insoluble in almost all the organic solvents except for the aprotic polar organic solvents and tetrahydrofuran, and thus has an excellent resistance against chemicals. Moreover, the film is tough and has a sufficient mechanical strength as indicated by a strength against rupture of 740 kg/cm^2 and an elongation at rupture of 4% which were measured at a tensile rate of 50 mm/min. and a temperature of 25°C.

Example 2

A poly(urethane/disiloxane) polymer was prepared in the same manner as in example 1 except that 2,4-tolylenediisocyanate (7.5 g, 0.043 mol) was used instead of diphenylmethanediisocyanate and that bis(hydroxypropyl)tetramethyldisiloxane (10.0 g, 0.040 mol) was used instead of bis(hydroxyethyl)tetramethyldisiloxane. The resultant polymer is represented by the above general formula, where

R^1 = ,

$R^2=CH_2$ and n=3, and has a logarithmic viscosity of 0.76. A film having a thickness of 15 µm was prepared based on the polymer in the same manner as in example 1. The film had a transmission coefficient of oxygen of 3.0×1.0^{-10}

CC(STP)·cm/cm^2·sec·cmHg and a separation coefficient of 5.7.

Example 3

A polymer was prepared in the same manner as in example 1 except that hexamethylenediisocyanate was used instead of diphenylmethanediisocyanate and that bis(hydroxybutyl)tetraphenyldisiloxane was used instead of bis(hydroxyethyl)tetramethyldisiloxane. The resultant polymer is represented by general formula (I) where R^1=-$(CH_2)_6$, R^2=-C_6H_5-, n=4, and has a logarithmic viscosity of 0.61. A film prepared based on the polymer in the same manner as in example 1 had a transmission coefficient of oxygen of 8.2x1.0^{-10} CC(STP)·cm/cm^2·sec·cmHg and a separation coefficient of 3.2.

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㊿気体分離膜

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㊼特許請求の範囲

1　一般式

$$-O\overset{\displaystyle O}{\overset{\|}{C}}NH-R^1-NH\overset{\displaystyle O}{\overset{\|}{C}}O(CH_2)_n\underset{\displaystyle R^2}{\overset{\displaystyle R^2}{\overset{|}{\underset{|}{Si}}}}-O-\underset{\displaystyle R^2}{\overset{\displaystyle R^2}{\overset{|}{\underset{|}{Si}}}}(CH_2)_n-$$

（但し、R^1は2価の脂肪族基又は芳香族基、R^2はそれぞれ独立に1価のアルキル基又は芳香族基、nは1～4の整数を示す。）

で表わされる繰返し単位を有するポリ（ウレタン／シロキサン）からなることを特徴とする気体分離膜。

発明の詳細な説明

本発明はシロキサン構造を含むポリウレタンからなる気体分離膜に関する。

近年、省資源、省エネルギーの観点から有機重合体膜による気体分離、特に空気の酸素富化が注目されているが、従来知られている酸素富化用膜は酸素の透過速度が小さすぎ、或いは窒素に対する酸素の透過係数比が小さいため、工業的な規模で酸素富化を行なうには適しない。例えばポリジメチルシロキサンは酸素の透過係数が10^{-8} cm³（STP）・cm/cm²・sec・cmHg台であつて、従来知られている重合体膜のなかでは最大であるが、窒素に対する透過係数比が精々2程度であつて、酸素の選択透過性又は分離性に劣り、高濃度の酸素を得ようとすれば多段の膜処理を要することとなり、装置、費用のいずれの点からも実用的でない。また、この膜は機械的強度が小さく、比較的厚い膜を用いる必要があり、従つて、透過係数は大きくとも、透過速度を大きくすることができない。

このため特公昭47-51715号公報にはポリビニルトリメチルシランからなる酸素富化膜が提案されており、酸素の窒素に対する透過係数比はポリジメチルシロキサンの約2倍に改善されているが、耐薬品性に劣り、空気中の汚染物質、ポンプ類からの油等により劣化しやすい欠点がある。また、米国特許第3189662号にはポリシロキサン－ポリカーボネートブロック共重合体が開示されているが、ポリカーボネート構造を含むために、ポリビニルトリメチルシラン膜同様に耐薬品性に劣る。

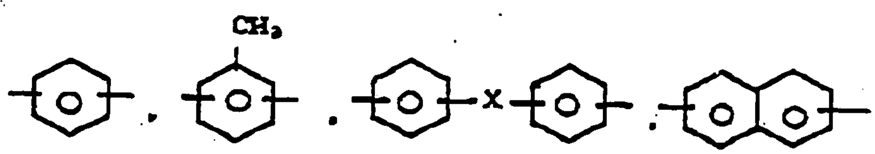
本発明者らは酸素の選択透過性、耐薬品性、機械的強度等にすぐれる気体分離膜について鋭意研究を重ねた結果、ポリウレタンの主鎖中にシロキサン構造を導入することにより上記要求に適う気体分離膜を得ることができることを見出し、本発明に至つたものである。

本発明による気体分離膜は一般式

$$-O\overset{\overset{\displaystyle O}{\|}}{C}NH-R^1-NH\overset{\overset{\displaystyle O}{\|}}{C}O(CH_2)_n\underset{\underset{\displaystyle R^2}{|}}{\overset{\overset{\displaystyle R^2}{|}}{Si}}-O-\underset{\underset{\displaystyle R^2}{|}}{\overset{\overset{\displaystyle R^2}{|}}{Si}}(CH_2)_n- \qquad (I)$$

(但し、R^1は2価の有機基、R^2はそれぞれ独立にアルキル基又は芳香族基、nは1～4の整数を示す。)
で表わされる繰返し単位を有するポリ(ウレタン/ジシロキサン)からなることを特徴とする。※

※一般式(I)において、R^1は2価の有機基、好ましくは脂肪族基又は芳香族基であり、ここに芳香族基はヘテロ原子を介して結合されていてもよい。従つて、これらの具体例として



$(CH_2)_6$—等を挙げることができ、ここにXは2価の有機結合基、即ち、原子価結合、アルキレン基又はヘテロ原子を含んでよい2価基であつて、具体例として$-CH_2-$，$-C(CH_3)_2-$，$-O-$，$-S-$等を挙げることができる。

R^2は1価のアルキル基又は芳香族基である。アルキル基は好ましくは炭素数が1～4である。R^2の特に好ましい具体例はメチル基又はフエニル基である。ジシロキサン構造は4つのR^2を有するが、すべてのR^2が同一である必要はない。

一般式(I)で表わされる繰返し単位を有するポリ(ウレタン/ジシロキサン)は一般式

$$OCN-R^1-NCO \qquad (II)$$

(R^1は前記と同じである。)
で表わされるジイソシアネートと、一般式

$$HO-(CH_2)_n\underset{\underset{\displaystyle R^2}{|}}{\overset{\overset{\displaystyle R^2}{|}}{Si}}-O-\underset{\underset{\displaystyle R^2}{|}}{\overset{\overset{\displaystyle R^2}{|}}{Si}}(CH_2)_n-OH \qquad (III)$$

(但し、R^2及びnは前記と同じである。)
で表わされるジシロキサン系ジオールとを通常の有機溶剤中にて加熱、反応させることによつて得られる。

上記一般式(II)で表わされるジイソシアネートにおいて、R^1は前記したとおりであり、好ましいジイソシアネートの具体例としてトリレンジイソシアネート、フエニレンジイソシアネート、ジフエニルメタンジイソシアネート、ジフエニルプロパンジイソシアネート、ジフエニルエーテルジイソシアネート、ナフタレンジイソシアネート、ヘキサメチレンジイソシアネート等を挙げることができる。

また、上記一般式(III)で表わされるジシロキサン系ジオールにおいて、R^2及びnは前記したとおりであり、一般に既に知られている方法によつて得ることができる。即ち、$n=1$の場合は米国特許第2527591号に、$n=2$及び3の場合はJ.Org.Chem.25，1637(1960)に、また、$n=4$の場合は米国特許第3083219号に開示されている。

上記ジイソシアネートとジシロキサンとを反応させるための反応溶剤は好ましくは、これら両者を共に溶解し得ると共に、これらに対して不活性

であり、且つ、生成するポリ（ウレタン／シロキサン）重合体をも溶解し得るものが用いられる。好ましい有機溶剤の具体例としてはジメチルスルホキシド、N−メチル−2−ピロリドン、N，N−ジメチルアセトアミド、N，N−ジメチルホルムアミド等の非プロトン性極性有機溶剤が挙げられ、一種又は二種以上の混合物が用いられ、好ましくは上記溶剤とメチルエチルケトン、メチルイソブチルケトン、シクロヘキサノン等の脂肪族、脂環族ケトン類との混合溶剤が用いられる。一般にジイソシアネートは上記非プロトン性極性有機溶剤に難溶性であるが、ケトン類との混合溶剤を用いることによりジオールとの反応を均一系又は均一系に近い状態で行なうことができる。

溶剤の使用量は特に制限されないが、ジイソシアネートとシロキサン系ジオールとの合計量が10〜50重量％、好ましくは20〜40重量％となるように用いられる。重合反応の温度は通常、50〜150℃の範囲であり、反応に要する時間は通常、数時間〜数十時間である。尚、高分子量の重合体を得るには、シロキサン系ジオールに対してジイソシアネートを2〜45モル％程度過剰に用いるのがよい。

このようにして得られるポリ（ウレタン／シロキサン）は通常、0.4〜1.2の対数粘度を有し、強靱な膜に形成することができる。この重合体は重合反応溶剤として例示したような前記極性溶剤及びテトラヒドロフランのような一部の環状エーテルを除き、ほとんどの有機溶剤に不溶性であつて、極めてすぐれた耐薬品性を有している。

本発明による気体分離膜は種々の方法によつて製造することができるが、普通は、上記ポリ（ウレタン／シロキサン）を製膜液溶剤に溶解して均一な製膜液とし、これを適宜の支持基材に流延塗布した後、加熱処理して溶剤を蒸発させて均質な膜とする。

気体の透過速度を大きくするためには膜厚は薄い程好ましいが、一方、機械的強度の点からは厚い方が好ましく、これらの観点から膜厚は0.05〜30μが望ましい。従つて、製膜液の重合体濃度は10重量％以下がよい。

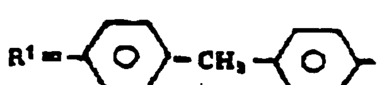
製膜液溶剤は重合反応溶剤と同様にジメチルスルホキシド、N−メチル−2−ピロリドン、N，N−ジメチルアセトアミド、N，N−ジメチルホルムアミド等の非プロトン性極性有機溶剤が好ましい。また、テトラヒドロフランもポリ（ウレタン／シロキサン）重合体をよく溶解するので製膜液溶剤として好適である。必要ならば上記非プロトン性有機溶剤及びテトラヒドロフランの混合溶剤も用いられる。製膜液を支持基材に塗布後、加熱する温度は製膜液溶剤にもよるが、上記非プロトン性極性有機溶剤の場合には80〜140℃、好ましくは100〜120℃である。特に好ましくはこのような温度範囲で溶剤のほとんど蒸発させた後、150℃程度に昇温して溶剤を完全に蒸発させる。製膜液溶剤としてテトラヒドロフランを用いた場合には常温でこれを蒸発させることができ、均質な膜を容易に得ることができる。

本発明の気体分離膜は以上のように主鎖にシロキサン構造を有するポリウレタンからなり、シロキサン構造の大きい酸素の透過速度とポリウレタン構造のすぐれた酸素の選択透過性、耐薬品性と相俟つて特に酸素富化に好適であり、更に機械的強度も大きいので、例えば空気の酸素富化の工業的実施に最適である。しかしながら、他の気体混合物の膜分離への使用を妨げるものではない。

以下に本発明の実施例を挙げるが、本発明はこれらに限定されるものではない。尚、以下の実施例において、気体の透過係数Pは25℃で高真空法により求めたものであり、分離係数αは25℃における当該気体の透過係数／窒素の透過係数（P_{N_2}）から求めたものである。

実施例 1

ビス（ヒドロキシエチル）テトラメチルジシロキサン（8.9g、0.040モル）のジメチルスルホキシド（27g）溶液をジフエニルメタンジイソシアネート（13.0g、0.052モル）のメチルイソブチルケトン（120g）溶液に加え、撹拌下に加熱した。徐々に粘度が上昇した。100℃の温度で5時間反応させて非常に粘稠な溶液を得た。この溶液を大量の水中に投じ、重合体を析出させ、水中で粉砕した。一夜放置後、重合体を濾別し、80℃で10時間真空乾燥した。得られた重合体は前記一般式(I)において


，$R^2 = CH_3$，

n＝2である繰返し単位を有し、対数粘度は0.88

であつた(N－メチル－2－ピロリドン、30℃、0.5 g/dl、以下同じ。)。

この重合体を5重量%のテトラヒドロフラン溶液とし、ヌズメッキ板上に流延した後、室温で3日間放置して溶剤を蒸発させ、次にヌズを水銀でアマルガムにして溶かし、厚み10 μの均質な重合体膜を得た。この重合体膜の気体透過性を高真空法にて測定し、結果を第1表に示す。

第 1 表

ポリ(ウレタン/ジシロキサン)膜の気体透過性

気 体	透過係数 P (CC(STP)・cm/cm²・sec・cmHg)	分離係数α
水 素	2.2×10^{-9}	47
ヘリウム	2.1×10^{-9}	45
二酸化炭素	1.4×10^{-9}	30
酸 素	2.8×10^{-10}	6
アルゴン	1.8×10^{-10}	4
窒 素	4.7×10^{-11}	1

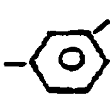
比較例として、実施例1においてビス(ヒドロキシエチル)テトラメチルジシロキサンの代わりにエチレングリコール(2.7 g、0.043モル)を用いた以外は実施例1と全く同様にしてポリウレタン膜を調製した。このポリウレタン膜の気体透過性を第2表に示す。

第 2 表

気 体	透過係数 P (CC(STP)・cm/cm²・sec・cmHg)	分離係数α
水 素	2.4×10^{-10}	308
ヘリウム	3.8×10^{-10}	490
二酸化炭素	2.7×10^{-11}	35
酸 素	5.8×10^{-12}	7
アルゴン	2.0×10^{-12}	3
窒 素	7.8×10^{-13}	1

以上の結果から、本発明のポリ(ウレタン/ジシロキサン)膜によれば酸素の窒素に対する分離係数を高く維持して、酸素の選択透過性を約50倍増大させることができた。更に、本発明の膜は前記非プロトン性極性有機溶剤及びテトラヒドロフランを除くほとんどすべての有機溶剤に不溶性であつて、耐薬品性に著しくすぐれるほか、引張速度50 mm/分、温度25℃にて測定した破断強度及び破断伸びはそれぞれ740 kg/cm² 及び4%であつて、膜は強靭で十分な機械的強度を有する。

実施例 2

実施例1においてジフエニルメタンジイソシアネートの代わりに2,4－トリレンジイソシアネート(7.5 g、0.043モル)を、また、ビス(ヒドロキシエチル)テトラメチルジシロキサンの代わりにビス(ヒドロキシプロピル)テトラメチルジシロキサン(10.0 g、0.040モル)を用いた以外は、実施例1と全く同様にして、前記一般式においてR¹＝——CH_3、R²＝CH_2、n＝3であつて、対数粘度0.76のポリ(ウレタン/ジシロキサン)重合体を得た。この重合体から実施例1と同様にして厚み15 μの膜を調製した。酸素の透過係数は 3.0×10^{-10} CC(STP)・cm/cm²・sec・cmHg、分離係数は5.7であつた。

実施例 3

実施例1においてジフエニルメタンジイソシアネートの代わりにヘキサメチレンジイソシアネートを、また、ビス(ヒドロキシエチル)テトラメチルジシロキサンの代わりにビス(ヒドロキシブチル)テトラフエニルジシロキサンを用いた以外は、実施例1と全く同様にして、前記一般式(I)において$R^1 = -(CH_2)_6-$, $R^2 = -C_6H_5-$, $n = 4$、対数粘度0.61の重合体を得た。この重合体から実施例1と同様にして得た膜は酸素の透過係数5.2×10^{-10} cc(STP)・cm/cm²・sec・cmHg、酸素の分離係数3.2であつた。

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